541.8

The University of Chicago
Founded by JOHN D. ROCKEFELLER

On Some Hydroxylamine Compounds

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

By MAXWELL ADAMS.

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

EASTON, PA.:
Press of The Chemical Publishing Co.
1902

3781
C53A
UNCLASSIFIED

The University of Chicago
Founded by JOHN D. ROCKEFELLER

On Some Hydroxylamine Compounds

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY MAXWELL ADAMS.

EASTON, PA.:
Press of The Chemical Publishing Co.
1902

Digitized by the Internet Archive
in 2025

https://archive.org/details/onsomehydroxylam0000maxw

On Some Hydroxylamine Compounds.

As a reagent in organic chemistry hydroxylamine has been carefully investigated, but from the standpoint of inorganic chemistry it has not received much attention, and the investigations in this field are in many places incomplete or contradictory. One reason for this neglect has been the cost and trouble of preparing it by the ordinary methods. These difficulties have now been overcome by the very economical and satisfactory method of Divers and Haga.[1]

The results obtained by Hofmann,[2] Rammelsberg,[3] and Pesci,[4] on the mercuramines, indicate a parallel line of work with hydroxylamine because of its relationship to ammonia.

The similarity of hydroxylamine to both water and ammonia indicates that through a study of it as a solvent some light might be thrown upon the part played by these liquids in crystallization. Pure hydroxylamine is a liquid above 33°; it might be used as a solvent in determining the electrolytic conductivity of solutions, and it would be interesting to note if it resembles water or ammonia in this particular.

The consideration of these facts, among others, led Dr. Lengfeld to suggest to me a study of hydroxylamine as a promising field for work. A review of the methods of preparation and estimation of hydroxylamine, its action on salts of mercury, and the properties of some of its halogen salts which have been hitherto overlooked, are considered in this article.

When the study was begun many conflicting statements were found, and it at once became evident that much work needed repetition, and a not inconsiderable part of this paper is devoted to a review of previous work. Attention was first directed towards the methods ordinarily used in the estimation of hydroxylamine; these were found inaccurate, and be-

[1] J. Chem. Soc. (London), **69**, 1665.
[2] Ann. Chem. (Liebig), **305**, 191.
[3] J. prakt. Chem., **38**, 558.
[4] Ztschr. anorg. Chem., **21**, 361.

fore any progress in this work could be made they had to be revised. Volumetric methods for the determination of hydroxylamine were first carried out in a systematic manner by Meyeringh,[1] who recommended three different processes :

1. The reduction of ferric sulphate with hydroxylamine and estimation of the ferrous sulphate with potassium permanganate.

2. The reduction of Fehling's solution.

3. The titration with free iodine solution in the presence of sodium phosphate or sodium bicarbonate.

All these methods have been employed by various chemists, some recommending one and some another. Knorre and Arndt,[2] in their work on the oxidation-products of hydroxylamine, use permanganate, and Lainer,[3] in his photographic work with hydroxylamine, employs the same reagent. This method was tested and found to be inaccurate. The amount of permanganate necessary for the titration was found to vary with the amount of ferric sulphate present, the length of time the solution was heated with the hydroxylamine, and the rapidity with which the permanganate was added.

Titration with free iodine in the presence of bicarbonate of sodium is used by Haga,[4] but this method has some defects. He finds that extreme dilution, or presence of carbonic acid, brings the results too high. The presence of other salts also influences the accuracy. In the present work the best results were obtained by titrating with standard iodine solution in the presence of sodium phosphate. When too great dilution is avoided and the relative proportions of the hydroxylamine and the sodium phosphate are kept fairly constant, concordant results are obtained. Wherever it was possible, however, the hydroxylamine was calculated indirectly from the nitrogen, which was determined by the Dumas method. The titration method was used to prove only that the nitrogen is not present as ammonia.

[1] Ber. d. chem. Ges., **10**, 1940.
[2] *Ibid.*, **33**, 30.
[3] Dingler: Polytech. J., **276**, 521.
[4] J. Chem. Soc. (London), **51**, 794.

The behavior of mercury salts towards hydroxylamine was first investigated by Dresler and Stein,[1] who tried the action of hydroxylamine on mercuric oxide and obtained free mercury, and Lossen,[2] who found that mercuric chloride was rapidly reduced by the same means. There is no doubt that this is true under certain conditions, but by varying the temperature and solvent several compounds of mercury with hydroxylamine may be obtained. A salt,

$$HgSO_4.(NH_2OH)_2.H_2O,$$

prepared by the action of hydroxylamine on mercuric sulphate, corresponds closely to the salts of cobalt, manganese, and nickel prepared by Feldt[3] and Uhlenhuth.[4] The chlorides of hydroxylamine and mercury, on the other hand, seem, as a rule, more complex. Crismer[5] and other chemists have prepared chlorides of zinc, cadmium, barium, cobalt, and manganese with hydroxylamine of crystallization. These compounds have the general formula $MCl_2(NH_2OH)_2$. Feldt,[6] in his effort to prepare the corresponding salt of mercury confirmed the statement of Lossen, Dressler, and others, that on account of the reducing action of hydroxylamine and the easy reduction of mercuric chloride, no stable addition-product is obtained. By modifying conditions of temperature and solvent, however, I have prepared and isolated a number of chlorides of mercury and hydroxylamine. The simplest of these, $HgCl_2(NH_2OH)_2$, corresponds in composition to the general type of the chlorides mentioned above. Further work, however, may show that it is analogous to the mercuramines. It forms a double salt with normal hydroxylamine hydrochloride, $HgCl_2.(NH_2OH)_2(NH_2OH.HCl)_2$, and also a double salt with dibasic hydroxylamine hydrochloride,

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl.$$

Besides these, a double salt of mercuric chloride with normal hydroxylamine hydrochloride, $HgCl_2(NH_2OH)HCl$, has been

[1] Ann. Chem. (Liebig), **150**, 242.
[2] *Ibid.*, Supp.-Bd., **6**, 220.
[3] Ber. d. chem. Ges., **27**, 401.
[4] Ann. Chem. (Liebig), **307**, 332.
[5] Bull. Chem. Soc., [3], **3**, 114.
[6] *Loc. cit.*

obtained, as well as a stable compound which may be mercuric chloride with dibasic hydroxylamine hydrochloride, $2HgCl_2.5(NH_2OH)_2HCl$, though it is probably much more complex.

Thinking that the other halogen salts of mercury and hydroxylamine might be less complex, I attempted to prepare them, but no compound with mercury and iodine was obtained, and only one bromide,

$$HgBr_2(NH_2OH)_2(NH_2OH.HBr)_2,$$

was prepared. The hydrobromide and hydriodide of hydroxylamine have a stronger reducing action upon mercury than the corresponding chloride, and they also appear to have less tendency to form complex salts. While Lossen[1] made a number of salts of hydroxylamine, and other chemists have since added to the number, no account of the hydrobromide has been given. Piloty and Ruff[2] prepared the tribasic hydroxylamine hydriodide, and Dunstan and Golding[3] made the dibasic hydriodide, but they were unable to obtain the normal hydriodide. I have prepared both the normal, $NH_2OH.HBr$, and the dibasic, $(NH_2OH)_2HBr$, hydroxylamine hydrobromides as well as the normal hydroxylamine hydriodide, $NH_2OH.HI$. As no double bromides or iodides of hydroxylamine with metallic salts corresponding to the general formula, $MX_2(NH_2OH)_2$, had been prepared, and since their action on mercury is too violent to separate any intermediate products of the reaction, it seemed desirable to study the action of hydroxylamine hydriodide and hydrobromide on cadmium salts, which, though similar to those of mercury, are less easily reduced. The compounds $CdBr_2(NH_2OH)_2$ and $CdI_2(NH_2OH)_3$ were readily obtained from this reaction.

Many experiments in this work required the use of pure, dry hydroxylamine. This was made from the phosphate by distillation according to the method of Uhlenhuth.[4]

[1] Ann. Chem. (Liebig), Supp.-Bd., **6**, 220.
[2] Ber. d. chem. Ges., **30**, 1656.
[3] J. Chem. Soc. (London), **69**, 839.
[4] Ann. Chem. (Liebig), **311**, 117.

EXPERIMENTAL PART.

Hydroxylamine sulphate, the starting point in the preparation of all the salts described below, is made according to the directions of Divers and Haga.[1] The following slight modifications, however, are observed in carrying out their method:

1. A constant supply of gas for sulphonating is obtained by using liquid sulphur dioxide confined in siphons.

2. If the solution into which the sulphur dioxide is being led contains 2 or less molecules of sodium carbonate to 1 molecule of sodium nitrite, the entire solution may decompose toward the end of the reaction, even though the vessel containing the solution is immersed in brine and ice. To avoid this a solution containing sodium carbonate in slight excess of the molecular proportions is employed. It was also found that, even if by mistake too little sodium carbonate has been added at the beginning, the decomposition could be arrested, if, as soon as the solution began to turn brown, sodium carbonate was added and sulphur dioxide run in until the solution became colorless. Taking these precautions the solution remains clear when it becomes acid, and may be warmed up rapidly with perfect safety.

3. After hydrolysis of the sodium oxamidosulphonate, $NH(OH)(SO_3Na)$, and the neutralization of the resulting sulphuric acid with sodium carbonate, it was found convenient to first cool the solution to zero and separate the principal portion of the sodium sulphate by crystallization, then to evaporate the remaining solution to such a volume that 1 cc. contains 0.25 gram of hydroxylamine sulphate, finally to cool this solution to —8°, and to remove the sodium sulphate which crystallizes. By this separation of the sodium sulphate into two portions the bulk of the solution is quickly reduced, the first and largest yield of sodium sulphate crystals is easily separated from hydroxylamine, and a concentrated solution of hydroxylamine sulphate is obtained which may be cooled to —8° without freezing.

[1] *Loc. cit.*

4. The final concentration of the solution containing the hydroxylamine sulphate is carried out at diminished pressure, thereby avoiding local superheating and decomposition.

Dry hydroxylamine sulphate is insoluble in absolute alcohol and almost insoluble in 95 per cent alcohol.

As in the course of this work it was necessary to know approximately the solubility of hydroxylamine sulphate in water at various temperatures, the following table, giving the amount of hydroxylamine sulphate in 1 gram water solution, was worked out; absolute accuracy was not attempted:

Temperature.	Grams of hydroxylamine sulphate.
—8°	0.307
0	0.329
10	0.366
20	0.413
30	0.441
40	0.482
50	0.522
60	0.560
90	0.685

Hydroxylamine Phosphate.—The phosphate of hydroxylamine is about one-twentieth as soluble in water at the ordinary temperature as the sulphate; hence when normal sodium phosphate is added to a concentrated solution of hydroxylamine sulphate, the phosphate separates in crystalline form, and it can be readily purified by recrystallization. Its solubility in water is as follows, the amount of the salt in 1 gram of the water solution being given:

Temperature.	Grams of hydroxylamine phosphate.
0°	0.012
10	0.015
20	0.019
30	0.027
40	0.040

Temperature.	Grams of hydroxylamine phosphate.
50	0.055
60	0.077
70	0.102
80	0.133
90	0.168

The difference in solubility between the phosphate and sulphate may be utilized to work up the mother-liquor and wash-waters from which the sulphate will no longer crystallize.

In the preparation of the sulphate by the Divers and Haga method, after two or three crops of crystals have been separated, there remains a viscous mother-liquor containing considerable hydroxylamine sulphate mixed with sodium sulphate, with impurities which were contained in the original crude materials, and with decomposition-products formed during the hydrolysis. From this mixture normal sodium phosphate precipitates a considerable amount of hydroxylamine phosphate.

The normal sodium phosphate for this purpose is readily prepared by adding the calculated quantity of sodium hydroxide to acid sodium phosphate. Including both the sulphate and phosphate, the yield of hydroxylamine obtained by this method is even better than that reported by Divers and Haga. Nine hundred grams of sodium nitrite gave 700 grams of sulphate and 80 grams of phosphate of hydroxylamine.

Hydroxylamine Hydrochloride, $NH_2OH.HCl$. — Eickhoff[1] states that if the calculated quantity of barium chloride be added to hydroxylamine sulphate in water solution and the barium sulphate removed by filtration, the hydroxylamine hydrochloride may be separated by concentration and crystallization. This method is difficult to carry out and the yield is poor. When either reagent is in excess double salts are formed, and if the hydroxylamine sulphate contains any impurities it is not easy to calculate the exact quantity of the chloride required for neutralization.

1 J. Pharm., [5], **21**, 245-246; Abstr. in J. Chem. Soc. (London), **58**, 558 (1890).

The following modification of the process is found to be much more satisfactory : Barium chloride is added in slight excess to a water solution of hydroxylamine sulphate, the solution filtered free from barium sulphate, and evaporated to dryness on a water-bath. The residue is placed in a Soxhlet apparatus and extracted with alcohol, the insoluble barium chloride remaining in the apparatus. The hydroxylamine hydrochloride, being only moderately soluble in alcohol, soon crystallizes in the distilling-flask, and that remaining in solution is easily obtained by evaporating the alcohol.

If chemically pure hydrochloride is desired, absolute alcohol should be used, taking precautions to exclude moisture, but for most purposes 95 per cent alcohol is satisfactory. The hydrochloride obtained in this way contains only a slight trace of barium. The phosphate being relatively insoluble in water can be easily purified by crystallization, and is also converted into the hydrochloride by the above process. This method is found convenient for reclaiming residues of hydroxylamine and reconverting them into the hydrochloride.

Hydroxylamine Hydrobromide, $NH_2OH.HBr$.—This salt is obtained as follows : Barium bromide is added to hydroxylamine sulphate in water solution, keeping the sulphate in slight excess, as barium bromide is not insoluble in alcohol. After filtering, the solution is evaporated to dryness on the water-bath, the residue dried in a vacuum desiccator over calcium chloride for forty-eight hours and extracted with absolute alcohol. On cooling the solution, large, well-formed, white, acicular crystals of hydroxylamine hydrobromide are deposited. A further yield of the salt is obtained, either by evaporating the alcoholic solution or by precipitating with ether. When the hydrobromide is precipitated from its alcoholic solution by ether, the crystals formed are shorter and the bases more prismatic than when crystallized by evapora-

tion. This salt is very soluble in water, insoluble in ether; pure and dry it is stable if kept in glass-stoppered bottles. In the presence of impurities it decomposes slowly in the light, becoming yellowish-brown in color. It is a stronger reducing agent than the corresponding hydrochloride.

I. 5 cc. solution containing 0.03135 gram substance required 6.8 cc. standard iodine solution (1 cc. iodine solution equals 0.00133 gram hydroxylamine).

II. 0.2913 gram substance gave 0.4799 gram AgBr and 0.0627 gram gave, on titration, 0.0182 gram hydroxylamine.

	Calculated for $NH_2OH.HBr$.	Found. I.	II.
Br	70.17	....	70.09
NH_2OH	29.02	28.86	28.92

Dibasic Hydroxylamine Hydrobromide, $(NH_2OH)_2HBr$.—This salt is prepared by adding free hydroxylamine to a concentrated alcoholic solution of the normal hydroxylamine hydrobromide. It separates as well-formed, white, plate-like crystals. A second crop of crystals separates upon the addition of a little ether to the filtrate. This compound is less soluble in alcohol at ordinary temperature than the normal salt. It is insoluble in ether and ligroin, very soluble in water. It acts as a strong reducing agent, and under normal conditions its properties are very similar to those of the corresponding dibasic hydrochloride. Analysis shows it to be $(NH_2OH)_2.HBr$.

0.2065 gram substance gave 0.2671 gram AgBr.

0.0513 gram required 17.3 cc. iodine solution.

	Calculated for $(NH_2OH)_2.HBr$.	Found.
Br	54.42	54.54
NH_2OH	44.89	44.87

Various proportions of free hydroxylamine were added to solutions of normal hydroxylamine hydrobromide in water and alcohol in an effort to prepare salts corresponding to the tribasic hydrochloride described by Lossen,[1] and the tribasic hydriodide prepared by Piloty and Ruff,[2] but without success.

[1] Ztschr. Chem. (N. F.), 7, 326.

[2] *Loc. cit.*

Hydroxylamine Hydriodide, $NH_2OH.HI$.—Dunstan and Golding[1] obtained the dibasic and tribasic hydroxylamine hydriodide by the action of methyl iodide on hydroxylamine dissolved in methyl alcohol. They also prepared both these salts by the direct combination of hydroxylamine and hydriodic acid, but when they attempted to prepare the normal hydriodide by mixing the calculated quantity of an alcoholic solution of hydroxylamine with aqueous hydriodic acid, the solution quickly darkened in color, and when it was evaporated either by heating it or by placing it in a desiccator over sulphuric acid, further decomposition occurred. Several other methods for preparing the hydriodide were tried by them without success.

Wolfenstein and Groll[2] have succeeded in making the normal hydriodide by treating free hydroxylamine with a water solution of hydriodic acid and evaporating the solution under diminished pressure. Their method was published after my work was done and it is, I believe, less satisfactory than mine, both as to the ease with which the operation is carried out and also in the yield obtained.

Normal hydroxylamine hydriodide is made by treating a solution of hydriodic acid in dry, low-boiling ligroin with pure hydroxylamine. Ligroin is chosen for this purpose as hydriodic acid attacks alcohol and ether. In making the hydriodic acid by the Lothar Meyer[3] method much time may be saved by keeping the flask containing the moistened iodine in ice-water while the phosphorus is being added. The addition of the phosphorus, which by the old method required a half hour or more, may in this way be accomplished in a few minutes. After the phosphorus is added the mixture is warmed to 40° or 45°, when a steady stream of gaseous hydriodic acid is evolved. This gas is thoroughly dried over calcium iodide[4] and phosphorus pentoxide, then conducted into dry ligroin at zero. On adding dry hydroxylamine to this solution, a violent reaction takes place and there is imme-

[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **34**, 2417.

[3] *Ibid.*, **20**, 3381.

[4] If calcium chloride is used as a drying agent, hydrochloric acid is found in the ligroin solution.

diately formed a white, crystalline precipitate of normal hydroxylamine hydriodide.

A direct analysis of the salt was not made, but after washing it thoroughly with ligroin it was dissolved in water and the proportion of the iodine to the hydroxylamine was found to be 1 molecule of hydroxylamine to 0.996 atom of iodine, which corresponds to the formula $NH_2OH.HI$ of the normal hydriodide.

10 cc. of a solution of the substance gave 0.7516 gram AgI, and 10 cc. of the same solution required 80.2 cc. iodine solution.

At the summer temperature this salt is very unstable, decomposing slowly under dry ligroin; even when placed over calcium chloride it gives off hydriodic acid and turns brown. It takes up moisture from the air and liquefies in a short time. Its water solution almost immediately turns light yellow in color because of a slight decomposition. It dissolves somewhat in ether, but the solution soon becomes cloudy and deposits dibasic hydroxylamine hydriodide. This reaction takes place much more rapidly if the hydroxylamine hydriodide is first dissolved in alcohol and ether is then added to the solution. When treated in this way, well-formed crystals of the dihydroxylamine hydriodide separate immediately and the solution becomes light-yellow in color. When free hydroxylamine is treated with a solution of ethyl iodide made by passing dry hydriodic acid into ether, according to the method of Silva,[1] there is formed dihydrohydroxylamine hydriodide with a considerable quantity of the tribasic hydriodide.

An attempt was made to prepare the normal hydroxylamine hydriodide by treating hydroxylamine sulphate in water solution with barium iodide, following out a method analogous to that by which the hydrochloride and hydrobromide have been prepared, but without success. The color and properties of the solution indicate that the salt was formed, yet when the solution was evaporated, either on the water-bath or under diminished pressure, it became dark in color, and when it was brought finally to dryness there remained free iodine mixed with crystals of some substance that was apparently the di-

[1] J., (1875), p. 250.

hydroxylamine hydriodide.[1] Not much work was done on this as the other method is much more satisfactory.

Sulphate of Mercury and Hydroxylamine, $HgSO_4(NH_2OH)_2H_2O$.—This salt is prepared by two methods :

1. To freshly precipitated mercuric oxide, washed free from alkali, hydroxylamine sulphate is added in considerable excess. When the mixture is vigorously shaken, the mercuric oxide dissolves entirely, producing a clear solution from which crystals soon separate. Care is taken to keep the solution cold and to avoid an excess of mercuric oxide.

2. To dry mercuric sulphate a 10 per cent solution of hydroxylamine sulphate in water is added and this mixture vigorously agitated, and then rapidly decanted from any undissolved mercuric sulphate. The clear liquid yields, on standing, crystals of the same salt as those made from the mercuric oxide. The crystals obtained by either of the above methods are purified by washing repeatedly with water acidified with sulphuric acid, and dried over phosphorus pentoxide.

Properties.—The salt is decomposed even in the cold by water, first turning a reddish-yellow and finally black. It may be kept in a desiccator over sulphuric acid, in the dark, for some time without undergoing any apparent change, but becomes colored upon exposure to light. When cold, it keeps under a solution containing a little free sulphuric acid or hydroxylamine sulphate, but when warmed to 55° it decomposes rapidly.

I. 0.3732 gram substance gave 0.1963 gram Hg.
0.2750 gram substance gave 0.1700 gram $BaSO_4$.
0.4387 gram substance gave 29 cc. N at 22° and 731.1 mm. (corr.)[2].

II. 0.4886 gram substance gave 0.2556 gram Hg.
0.4519 gram substance gave 0.2774 gram $BaSO_4$.

[1] The work described here was carried on during the month of July, when the temperature was between 30° and 40° and the atmosphere almost saturated with water vapor. In evaporating at diminished pressure a temperature below 30° was not obtained. The method is similar to that successfully employed by Wolfenstein and Groll.

[2] Corrected for vapor-tension over 30 per cent caustic potash.

0.3812 gram substance gave 24 cc. N at 22° and 732.2 mm. (corr.).

III. 0.4705 gram substance gave 0.2467 gram Hg.
0.1822 gram substance gave 0.1117 gram $BaSO_4$.

	Calculated for $HgSO_4(NH_2OH)_2.H_2O$.	Found. I. Made from oxide.	II.	III. Made from sulphate.
Hg	52.63	52.57	52.51	52.41
SO_4	25.26	25.48	25.29	25.28
N	7.36	7.36	7.09	....

Chlorides of Mercury and Hydroxylamine, $HgCl_2(NH_2OH)_2$. —The compound $HgCl_2(NH_2OH)_2$ is prepared by the following methods:

1. A cold alcoholic solution of hydroxylamine is added, drop by drop, to a thoroughly agitated solution of mercuric chloride in absolute alcohol, which is cooled to —10°.

2. Free hydroxylamine is added, drop by drop, to a mixture of 4 parts of mercuric chloride and 1 part hydroxylamine hydrochloride, dissolved in alcohol, which is cooled to —10°.

On allowing the solutions produced by either of the above methods to remain cold for a few minutes, white microscopic crystals of $HgCl_2(NH_2OH)_2$, mixed with mercurous chloride and double salts of $HgCl_2(NH_2OH)_2$ with hydroxylamine hydrochloride, separate. By filtering, washing, and redissolving in absolute alcohol, to which has been added a trace of hydroxylamine hydrochloride, long, white, acicular crystals of $HgCl_2(NH_2OH)_2$ are obtained. The second of the above methods gives the better results, as there is less mercurous chloride formed.

I. 0.2152 gram substance gave 0.1290 gram Hg.
0.2977 gram substance gave 0.2495 gram AgCl.
0.3453 gram substance gave 23.8 cc. N at 17° and 735.2 mm. (corr.).

II. 0.0945 gram substance gave 0.0560 gram Hg.
0.1718 gram substance gave 0.1467 gram AgCl.
0.2054 gram substance gave 15 cc. N at 18° and 740.2 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2$.	Found. I. Salt made by 1st method.	Found. II. Salt made by 2nd method.
Hg	59.34	59.98	59.25
Cl	21.06	20.97	21.11
N	8.39	7.97	8.21

This substance is fairly soluble in methyl or ethyl alcohol, from which solution it may be precipitated by ether. On standing in absolute alcohol there is considerable reduction even in the cold, while on warming the reduction is much more rapid. The stability of this salt is increased by the presence of a small quantity of hydroxylamine hydrochloride. Sodium hydroxide decomposes it rapidly. It is insoluble in ether, but readily soluble in a water solution of hydroxylamine hydrochloride, with which it probably forms a double salt. It is immediately decomposed by water into mercurous chloride. The crystals keep their shape, although, under a microscope, they are found to be lusterless and porous. When fresh crystals of this substance are dissolved in alcohol or a water solution of hydroxylamine hydrochloride, and ammonia is added to the solution, a white precipitate is formed which becomes black on standing a few minutes in the cold, or immediately on warming. This change of color is accompanied by an evolution of gas, and finally gray metallic mercury collects.

$HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.—One molecule of mercuric chloride and 2 molecules of hydroxylamine hydrochloride are dissolved in absolute methyl alcohol, cooled down to —10°, and 2 molecules of free hydroxylamine are added, as in the method described in the previous experiment. A white, crystalline substance is thus obtained which in form differs from that previously described. The crystals are much more dense, and may be recrystallized from methyl alcohol without change of composition, as is shown by analysis II. below. They are soluble in ethyl and methyl alcohol, and appear to be the most stable of any of the mercury compounds here described, yet upon warming considerable decomposition takes place. They are unstable in the presence of alkalies, either in a solution of water or alcohol.

I. 0.3132 gram substance gave 0.1336 gram Hg.
0.2372 gram substance gave 0.2843 gram AgCl.
0.3410 gram substance gave 36.2 cc. N at 16° and 731.2 mm. (corr.).

II. 0.1456 gram substance gave 0.0615 gram Hg.
0.2224 gram substance gave 0.2669 gram AgCl.

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH.HCl)_2$.	Found. I. Crude.	II. Recrystallized.
Hg	42.12	42.67	42.28
Cl	29.83	29.64	29.68
N	11.77	12.16	....

$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.—One molecule of mercuric chloride and 1 molecule of hydroxylamine hydrochloride are dissolved in methyl alcohol, cooled to —10°, and 3 molecules of free hydroxylamine contained in a concentrated solution of cold methyl or ethyl alcohol are slowly added with constant shaking. The solution remains clear for a few minutes, but when left standing for half an hour in brine and ice a considerable quantity of white crystals, which under the microscope appear uniform, separates. This salt is soluble in methyl and ethyl alcohol. Water also dissolves it completely, but the solution becomes turbid on standing a few minutes.

I. 0.2284 gram substance gave 0.1043 gram Hg.
0.2094 gram substance gave 0.2036 gram AgCl.
0.2610 gram substance gave 29.4 cc. N at 20° and 728 mm. (corr.).

II. 0.2365 gram substance gave 0.1078 gram Hg.
0.2802 gram substance gave 0.2751 gram AgCl.
0.4692 gram substance gave 49.8 cc. N at 19° and 741 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)_2(NH_2OH)_2HCl$.	Found. I. From methyl alcohol.	II. From ethyl alcohol.
Hg	45.50	45.68	45.58
Cl	24.23	23.96	24.28
N	12.74	12.66	12.24

An attempt to recrystallize this substance from alcohol

shows that on warming there is considerable reduction into mercurous chloride, and when the solution is filtered and cooled, long, white crystals are obtained which, when analyzed, prove to be $HgCl_2(NH_2OH)_2$.

In analyzing the compound

$$HgCl_2(NH_2OH)_2(NH_2OH)_2HCl,$$

approximately one-half of the nitrogen is driven off at a low temperature, while to expel the remainder it is necessary to elevate the temperature very considerably, which indicates that the nitrogen is held bound in two different combinations which are expressed by the double-salt formula given above.

Other double salts of this nature were obtained, but when an attempt was made to purify them they decomposed completely or changed into the more stable forms before they could be separated.

Double Chloride of Mercury and Hydroxylamine, $HgCl_2(NH_2OH)HCl$. — Hydroxylamine hydrochloride increases the solubility of mercuric chloride in alcohol or water, and a double salt is prepared by mixing hydroxylamine hydrochloride and mercuric chloride in the proportion of 1 molecule of each dissolved in as small an amount of water as possible. The solution is then placed over calcium chloride. In a few days white crystals of a double salt,

$$HgCl_2.(NH_2OH)HCl,$$

separate. The salt thus obtained is filtered by suction and dried on blotting-paper. Owing to its extreme solubility in both alcohol and water, it is difficult to purify. It is less soluble in ether, but when the solution is evaporated it separates as an oil and not as crystals. A sample left exposed to the air absorbed water and liquefied in an hour.

0.4585 gram substance gave 0.2710 gram Hg.

0.3712 gram substance gave 0.4719 gram AgCl.

0.7132 gram substance gave 24.3 cc. N at 17° and 738 mm. (corr.).

	Calculated for $HgCl_2(NH_2OH)HCl$.	Found.
Hg	58.73	59.10
Cl	31.25	31.98
N	4.11	3.94

When mercuric chloride is added to hydroxylamine hydrochloride in excess of the proportion of 1 : 1, and the solution is evaporated, mercuric chloride separates from the hydroxylamine ; and when in a proportion of less than 1 : 1, hydroxylamine hydrochloride separates free from mercury. If other salts are formed they dissociate upon concentration and cannot be obtained in this way. Hydroxylamine hydrochloride is almost insoluble in absolute ether. An attempt was made to prepare double salts by using ether as a solvent for mercuric chloride and adding powdered hydroxylamine hydrochloride to the solution in various proportions, but without success, for when 2.2 grams of hydroxylamine hydrochloride are added to 4.4 grams of mercuric chloride dissolved in 300 cc. of absolute ether, only 0.32 gram of hydroxylamine hydrochloride is dissolved after shaking the mixture for three days. When a small quantity of alcohol is present the solubility of the hydroxylamine hydrochloride is greatly increased, and when ligroin is added a voluminous white precipitate is produced. Analysis shows this to be a mixture which proved so unstable that no definite pure salt could be obtained.

$2HgCl_2.5(NH_2OH)_2HCl$.—This appears to be the most easily prepared of any of the mercury and hydroxylamine compounds here described. Apparently, whenever mercuric chloride is present in solution with excess of hydroxylamine hydrochloride and free hydroxylamine, this salt is formed. The compound, besides occurring as a by-product in several other experiments, is prepared in the following ways :

1. There is added to freshly prepared mercuric oxide, suspended in ethyl alcohol, a solution of hydroxylamine hydrochloride in ethyl alcohol. Both liquids are cooled down to —10° in brine and ice, mixed while cold, shaken thoroughly, and decanted from the undissolved mercuric oxide. The clear solution, on standing a few minutes, deposits flat, hexagonal crystals which must be immediately separated from the solution containing undissolved mercuric oxide. If they are left in contact with the oxide, reduction begins at once and spreads rapidly through all the crystals, leaving, finally, metallic mercury. By keeping the temperature below zero

this decomposition is retarded, but not wholly prevented. The crystals thus obtained are further purified by recrystallization from absolute alcohol (see Analysis I.).

2. A solution of hydroxylamine hydrochloride in methyl alcohol is added to mercuric oxide suspended in methyl alcohol. Crystals separate, similar in appearance to those separating from ethyl alcohol. The salt is more soluble in methyl alcohol than in ethyl alcohol, and decomposes more easily in the presence of the former. For the composition of these crystals see analysis II.

3. Two parts of free hydroxylamine are added to a mixture, in alcohol, of 1 part of mercuric chloride with 6 of hydroxylamine hydrochloride; by keeping all the solutions below zero, crystals similar to those previously described separate. They are purified by recrystallization. It will be seen that this method is similar to that used by Hofmann[1] for preparing his mercuramines (analysis III.).

4. The alcoholic filtrate from which the first crop of crystals separates contains in solution a considerable quantity of the same salt which may be precipitated by adding ether. The crystals thus formed are similar to those previously obtained (analysis IV.).

5. This same salt of mercury is obtained by adding a solution of hydroxylamine hydrochloride in water to mercuric oxide; but on account of the solubility of the salt, as well as its instability in water, this method is less satisfactory than those previously described.

I. 0.4425 gram substance gave 0.1680 gram Hg.
0.4752 gram substance gave 0.5860 gram AgCl.
0.4860 gram substance gave 55 cc. N at 20° and 737 mm. (corr.).

II. 0.5078 gram substance gave 0.1931 gram Hg.
0.3883 gram substance gave 0.4771 gram AgCl.
0.3246 gram substance gave 38 cc. N at 19° and 740.1 mm. (corr.).

III. 0.2488 gram substance gave 0.0938 gram Hg.
0.2085 gram substance gave 0.2587 gram AgCl.

[1] *Loc. cit.*

0.2385 gram substance gave 28.1 cc. N at 21°.5 and 733 mm. (corr.).

IV. 0.1718 gram substance gave 0.0651 gram Hg. 0.2129 gram AgCl.

	Calculated for $2HgCl_2.5(NH_2OH)_2HCl$.	Found. I.	II.	III.	IV.
Hg	37.95	37.96	38.02	37.72	37.88
Cl	30.26	30.28	30.38	30.48	30.29
N	13.28	12.48	13.17	13.28	....

The salt is soluble in water at the ordinary temperature with gradual reduction to mercurous chloride. When ammonium hydroxide is added to a water solution, a white precipitate is formed which turns black gradually in the cold, and rapidly when heated. It is soluble in alcohol and ether; in the presence of mercuric oxide it decomposes slowly at —10°, and rapidly at higher temperatures. It is soluble in hydrochloric acid. The slightest trace of alkali causes decomposition.

Some experiments were carried out with mercurous chloride and hydroxylamine to determine whether a reaction takes place between them, but owing to the insolubility of the mercurous chloride no definite results were obtained. Freshly precipitated mercurous chloride, when treated with a solution of hydroxylamine hydrochloride, was found to be slightly soluble in it, but no combination of the two was observed. Mercurous chloride, when boiled with free hydroxylamine in methyl alcohol in a flask fitted with a return condenser, was reduced gradually to metallic mercury. In the cold the reduction takes place very slowly.

Mercuric Bromide and Hydroxylamine.—When mercuric oxide is treated with a solution of normal hydroxylamine hydrobromide in an alcoholic solution cooled below zero, it dissolves, and if the solution is kept cool there separate white, well-formed crystals of dihydroxylamine hydrobromide. The solution contains mercuric bromide, which can be separated. The reaction is probably represented by the following equation:

$$HgO + 4NH_2OH.HBr = HgBr_2 + 2(NH_2OH)_2HBr + H_2O.$$

This is in marked contrast with the action of hydroxylamine hydrochloride on mercuric oxide.

$HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.—This compound is made by mixing mercuric bromide and normal hydroxylamine hydrobromide in the proper molecular proportions in methyl alcohol, cooling the mixture below zero, and adding to it, drop by drop, a solution of free hydroxylamine in methyl alcohol. On the addition of ether a white precipitate is formed, which is filtered and washed thoroughly with ether, care being taken to keep the salt cold. Analysis shows it to be $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$. It crystallizes in microscopic, quadratic plates. It is soluble in methyl alcohol with slow decomposition. The water solution becomes cloudy on standing a few minutes, indicating a reduction to mercurous bromide. It is readily decomposed by alkalies and is less stable than the corresponding chloride.

0.3911 gram substance gave 0.1189 gram Hg.

0.2879 gram substance gave 0.3326 gram AgBr.

0.1838 gram substance gave 14.4 cc. at 28° and 726.2 mm. (corr.).

	Calculated for $HgBr_2(NH_2OH)_2.(NH_2OH.HBr)_2$.	Found.
Hg	30.58	30.42
Br	48.93	49.16
N	8.56	8.84

Methods similar to those by which $HgCl_2(NH_2OH)_2$ was obtained were tried to prepare the corresponding bromide, but without success.

Mercuric Iodide and Hydroxylamine.—When mercuric oxide was treated with hydroxylamine hydriodide the reduction to metallic mercury was so rapid, even in the cold, that no intermediate products could be separated.

Mercuric iodide was dissolved in alcohol and cooled below zero; to this solution hydroxylamine hydriodide was added. Yellow crystals of pure mercurous iodide soon separated. Attempts were made to precipitate some salt from the solution with ether and ligroin before the mercurous iodide separated, but without success. When these results are compared with

those obtained with the hydroxylamine hydrochloride and hydrobromide, an increase in reducing power from the hydrochloride to the hydriodide is noted.

Cadmium Bromide and Hydroxylamine.—Hydroxylamine combines with neither mercuric iodide nor bromide to form stable salts of the general formula $MX_2(NH_2OH)_2$. Attention was turned, therefore, toward cadmium, since its salts are in some respects similar to mercury, yet less easily reducible. Cadmium bromide was dissolved in alcohol, and to the solution free hydroxylamine was added. There was immediately formed a fine, white, crystalline precipitate of $CdBr_2(NH_2OH)_2$. This salt dissolves in hot water, forming in a few minutes a white, basic salt. It is readily soluble in dilute acids, insoluble in alcohol and ether.

0.2316 gram substance gave 0.1418 gram $CdSO_4$.

0.3965 gram substance gave 0.4404 gram AgBr.

0.0546 gram substance gave, on titration, 0.0105 gram NH_2OH.

0.3252 gram substance gave 24.6 cc. N at 27° and 721 mm. (corr.).

	Calculated for $CdBr_2(NH_2OH)_2$.	Found.
Cd	33.13	32.94
Br	47.33	47.26
NH_2OH	19.52	19.22
N	8.28	8.13

Cadmium Iodide and Hydroxylamine, $CdI_2(NH_2OH)_3$.—Pure hydroxylamine is added to a strong solution of cadmium iodide in alcohol. A precipitate, which dissolves readily, is formed when the addition is first made; but on allowing the solution to stand there separate large, colorless, acicular crystals of $CdI_2(NH_2OH)_3$.

0.2886 gram substance gave 0.1284 gram $CdSO_4$.

0.4155 gram substance gave 0.4185 gram AgI.

0.0916 gram substance gave, on titration, 0.0197 gram NH_2OH.

0.2456 gram substance gave 20.4 cc. N at 26° and 722 mm. (corr.).

	Calculated for $CdI_2(NH_2OH)_3$.	Found.
Cd	24.08	23.96
I	54.57	54.44
NH_2OH	21.29	21.52
N	9.03	9.08

This compound is stable, soluble in both alcohol and water, and insoluble in ether. Its formula emphasizes the tendency of iodine, already noted by Dunstan and Golding,[1] to combine with 3 molecules of hydroxylamine.

Analytical Methods.

The mercury in the preceding experiments was determined by dissolving the compounds in potassium cyanide, passing an electric current of 0.1 ampère and 2.5 volts for fourteen hours through the solution and weighing the metallic mercury.

For estimating the chlorine in those salts which are soluble without decomposition in water, the solution was slightly acidified with nitric acid and the mercury removed by means of hydrogen sulphide. By keeping it in a warm place for a few hours most of the hydrogen sulphide is driven off; silver nitrate added to the solution made alkaline with ammonia removes the remainder; then, on making the solution acid, the silver chloride is precipitated and determined in the usual manner. Though this method might have given good results with those chlorides which are insoluble or give precipitates in water, it was considered safer to heat them in a tube with calcium oxide, drive off the mercury, and determine the chlorine in the residue.

In the analysis of those salts containing sulphuric acid, a weighed quantity of the substance was fused with sodium carbonate and potassium nitrate to remove the mercury, and the residue treated with water and barium chloride in the usual manner.

I wish here to express my thanks to Dr. Felix Lengfeld, at whose suggestion and under whose careful help and guidance this work was carried out.

Kent Chemical Laboratory,
University of Chicago,
August 24, 1901.

[1] *Loc. cit.*